

119464

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

10/019161

INTERNATIONAL APPLICATION NO.
PCT/FR00/01692

INTERNATIONAL FILING DATE
20 June 2000 (20-06-00)

PRIORITY DATE CLAIMED
21 June 1999 (21.06.99)

TITLE OF INVENTION HYDROPHOBIC CATIONIC DISPERSIONS STABILIZED BY MALEIMIDE COPOLYMERS OF LOW MOLECULAR MASS, FOR THE SIZING OF PAPER

APPLICANT(S) FOR DO/EO/US BETREMIEUX Isabelle, DUMOUSSEAUX Christophe, VERGE Christophe, FERET Bruno, FIAT Jean-Jacques

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☒ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:

Translation of Amendments to claims under PCT Article 19 are enclosed as AMENDED SHEET pages 21 to 23. All of the claims are being amended via enclosed preliminary Amendment.

| | | | | | | | |
|--|--------------|--------------|---|---|--|----------------------------------|--|
| U.S. APPLICATION NO. (if known, see 37 CFR 1.53) 10/019161 | | | INTERNATIONAL APPLICATION NO. PCT/FR00/01692 | | | ATTORNEY'S DOCKET NUMBER | |
| 17. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) : Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$970.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$840.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$690.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$670.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$96.00 <div style="text-align: right;">ENTER APPROPRIATE BASIC FEE AMOUNT =</div> | | | | | | CALCULATIONS PTO USE ONLY | |
| Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)). | | | | | | \$ | |
| CLAIMS | NUMBER FILED | NUMBER EXTRA | RATE | | | | |
| Total claims | - 20 = | 0 | X \$18.00 | \$ | | | |
| Independent claims | 1 - 3 = | 0 | X \$78.00 | \$ | | | |
| MULTIPLE DEPENDENT CLAIM(S) (if applicable) | | | + \$260.00 | \$ | | | |
| TOTAL OF ABOVE CALCULATIONS = | | | | \$ | | | |
| Reduction of 1/2 for filing by small entity, if applicable. A Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28). | | | | \$ | | | |
| SUBTOTAL = | | | | \$ | | | |
| Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). | | | | \$ | | | |
| TOTAL NATIONAL FEE = | | | | \$ 840 | | | |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property | | | | \$ | | | |
| TOTAL FEES ENCLOSED = | | | | \$ 840 | | | |
| | | | | Amount to be | | \$ | |
| | | | | refunded: | | \$ | |
| | | | | charged: | | \$ | |
| | | | | | | | |
| a. <input type="checkbox"/> A check in the amount of \$_____ to cover the above fees is enclosed. b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>501275</u> in the amount of \$ <u>840</u> to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>501275</u> . A duplicate copy of this sheet is enclosed. | | | | | | | |
| NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status. | | | | | | | |
| SEND ALL CORRESPONDENCE TO Michael B. Fein Cozen O'Connor 1900 Market Street Philadelphia, PA 19103 | | | | <div style="text-align: center;"> </div> <div style="text-align: center;"> SIGNATURE Michael B. Fein <hr/> NAME 25,333 <hr/> REGISTRATION NUMBER </div> | | | |

UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Isabelle **BETREMIEUX**

Christophe DUMOUSSEAUX

Christophe VERGE

Bruno FERET and

Jean-Jacques FLAT

FOR: : Hydrophobic Cationic Dispersions Stabilized by
Maleimide Copolymers of Low Molecular Mass,
for the Sizing of Paper

Serial No. : N/A

Filing Date : N/A

Attorney Docket : 119464

Assistant Commissioner for Patents
Washington, DC 20231

PRELIMINARY AMENDMENT

Prior to the Examination of the accompanying U.S. National Stage Application of PCT
Application PCT/FR00/01692 please amend as follows.

IN THE SPECIFICATION

Page 1, before line 4, insert as new line -- BACKGROUND OF THE INVENTION --

Page 5, before line 8, insert as new line -- SUMMARY OF THE INVENTION --

Page 6 before line 15, insert as new line -- DETAILED DESCRIPTION --

IN THE CLAIMS

Amend claims 1 to 11 and add claims 12 to 18 as set forth in the following Clean Copy of

Amended Claims.

CLEAN COPY OF AMENDED CLAIMS

1. Process for producing an aqueous cationic dispersion of polymers having hydrophobic characteristics comprising emulsion polymerizing at a temperature ranging from 30 to 100°C one or more monomers in the presence of 30 to 50% by weight, with respect to the one or more monomers, of a surfactant consisting of imidized styrene/maleic anhydride copolymer, the solids content of the dispersion being 20 to 50%.

2. Process according to claim 1 wherein the weight ratio of styrene to maleic anhydride of the copolymer is about 1/1 to 6/1.

3. Process according to claim 2 wherein the ratio is 2/1 to 4/1.

4. Process according to claim 1 wherein the copolymer has a number average molecular weight of about 500 to 20,000.

5. Process according to claim 4 wherein the number average molecular weight is 2000 to 5000.

6. Process according to claim 1 wherein the copolymer has a degree of imidization of about 50 to 100%.

7. Process according to claim 1 wherein the copolymer is imidized by dimethylpropylene diamine.

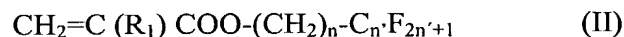
8. Process according to claim 1 wherein the monomer(s) are one or more of either (A) hydrophobic monomers selected from the group consisting of

(i) alkyl (meth)acrylates of the formula (I):



wherein $\text{R}_1 = \text{H}$ or CH_3 , and R_2 is a group having 1 to 22 carbon atoms;

(ii) perfluoroalkyl (meth)acrylates of formula (II):



wherein $R_1 = H$ or CH_3 ; $n = 1-4$; and $n' = 1-14$;

- (iii) vinyl acetate;
- (iv) styrene; and
- (v) versatic esters; and

(B) hydrophilic monomers.

9. Process according to claim 8 wherein the monomer(s) comprise one or more hydrophobic monomers selected from the group consisting of methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, and methyl methacrylate;

10. Process according to claim 8 wherein the monomer(s) comprise one or more relatively hydrophilic monomers selected from the group consisting of acrylic acid, methacrylic acid, acrylamide, and ethylene glycol (meth)acrylate.

11. Composition comprising an aqueous cationic dispersion prepared by process of claim 1.

12. Composition of claim 11 wherein the dispersed emulsion polymer particles have a size of about 50 to 500 nm.

13. Composition of claim 12 wherein the particle size is about 50 to 300 nm.

14. Composition of claim 11 wherein the dispensed emulsion polymer has a glass transition temperature of about -70°C to 100°C.

15. Composition of claim 11 wherein the glass transition temperature is about 0 to 50°C.

16. Process of treating paper or boards comprising using the composition of claim 11 as an internal sizing agent.

17. Process of claim 16 wherein no retention agent is used and immediate sizing is obtained.

18. Process of claim 16 wherein one or more additional sizing agents are used as surface sizing agents.

19. Process of claim 18 wherein the additional sizing agent(s) are selected from starches.

20. Composition useful for external sizing or internal sizing of paper or board comprising (A) an aqueous cationic dispersion prepared according to claim 1 and (B) starch in a weight ratio of (A) to (B) of about 5:95 to 50:50.

REMARKS

Claims 1 to 20 are in the case.

Claims 1 to 11 were presented in an amendment under Article 19 in the PCT Application from which the present application claims priority. The claims have all been rewritten to put them in a form more appropriate to U.S. practice. Each of the claims finds basis in the original claims and the specification.

Respectfully Submitted,

COZEN O'CONNOR

By: Michael B. Fein

Michael B. Fein, Esquire
Reg. No. 25,333
The Atrium
1900 Market Street
Philadelphia, PA 19103
(215) 665-4622(v)
(215) 701-2246 (f)
mfein@cozen.com

PHILA1\1546864\5 099991 000

CLAIMS

1. Process for producing an aqueous cationic dispersion of polymers with a hydrophobic nature based on the emulsion polymerization at a temperature ranging from 30 to 100°C of at least one emulsion-polymerizable monomer in the presence of 30 to 50% by weight, with respect to the monomer(s), of an imidized styrene/maleic anhydride copolymer acting as sole surfactant, the solids content of the dispersion being from 20 to 50%.

2. Process according to Claim 1, characterized in that the styrene and the maleic anhydride of the said copolymer are taken in a ratio of 1/1 to 6/1 and preferably of 2/1 to 4/1.

3. Process according to Claim 1 or 2, characterized in that the said copolymer has a number-average molecular mass of between 500 and 20,000 and preferably between 2000 and 5000.

4. Process according to one of the preceding claims, characterized in that the degree of imidization of the said copolymer is between 50 and 100%.

5. Process according to one of the preceding claims, characterized in that the said copolymer is imidized by dimethylpropylenediamine.

6. Process according to any one of the preceding claims, characterized in that the monomer is chosen from the groups comprising:

- hydrophobic monomers, such as methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate and more generally alkyl (meth)acrylates of formula:

$\text{CH}_2=\text{C}(\text{R}_1)\text{COOR}_2$, with $\text{R}_1=\text{H}$ or CH_3 and R_2 a group comprising 1 to 22 C,

perfluoroalkyl (meth)acrylates of formula:

$\text{CH}_2=\text{C}(\text{R}_1)\text{COO}-(\text{CH}_2)_n-\text{C}_{n'}\text{F}_{2n'+1}$, with $\text{R}_1=\text{H}$ or CH_3 , $n=1-4$ and $n'=1-14$,

vinyl acetate, styrene or versatic esters,

- relatively hydrophilic monomers, such as acrylic acid, methacrylic acid, acrylamide or ethylene glycol (meth)acrylate.

7. Cationic dispersion of polymers with a hydrophobic nature as can be had by the process of Claims 1 to 6, characterized in that the polymer particles have a size of between 50 and 500 nm and preferably of less than 300 nm.

8. Dispersion according to Claim 7, characterized in that the polymer with a hydrophobic nature has a glass transition temperature of between -70°C and 100°C and preferably between 0 and 50°C .

9. Use of the dispersion according to Claim 7 or 8 as internal sizing agent in the treatment of papers and boards.

10. Use of the dispersion according to Claim 7 or 8 in combination with other sizing agents, such as starch, in the surface sizing of papers and boards.

11. Composition for the external sizing of papers and boards comprising the dispersion according to either of Claims 7 and 8 and starch taken in a ratio by mass ranging from 5 to 50%.

**HYDROPHOBIC CATIONIC DISPERSIONS STABILIZED
BY MALEIMIDE COPOLYMERS OF LOW MOLECULAR
MASS, FOR THE SIZING OF PAPER**

The present invention relates to the field of
5 the sizing of paper and in particular to sizing agents
based on an aqueous cationic dispersion of hydrophobic
polymers. It also relates to the process for producing
such dispersions.

A good sizing agent is desired for every kind
10 of paper, in particular printing and writing paper,
paper for labels, wastepaper and wrapping paper.

Two kinds of sizing agents generally exist:
surface or internal sizing agents. The term "surface
sizing agent" is understood to mean an agent applied at
15 the surface of papers, generally in conjunction with
starch, using a size press; on the other hand, the term
"internal sizing agent" is understood to mean an agent
added with the fibres in the wet part of the
manufacture of the paper.

20 A good surface sizing agent allows paper
manufacturers to obtain a paper with good resistance to
water while reducing and even sometimes eliminating
internal sizing, which requires a larger amount of
product than surface sizing. It also makes it possible
25 to obtain a paper with good surface properties, which
are particularly important in obtaining good
printability properties on papers.

It is now known to a person skilled in the art to use, as surface sizing agent, emulsified or dispersed polymers, in combination with starch, in preference to dissolved polymers. They make it possible
5 to obtain sizing agents having a high solids content with a low viscosity. They cause less of a foaming problem than dissolved polymers of the styrene-acrylic acid or styrene-maleic anhydride type, for example. These dispersions can be anionic or cationic, the
10 latter being less common and more difficult to synthesize.

As far as internal sizing agents are concerned, a person skilled in the art is looking for a product which can be used without a retention agent and
15 without a maturing stage. The commonest internal sizing agents are alkyl ketene dimer (AKD), alkyl succinic anhydrides (ASA) and colophonies. They are not suitable under all manufacturing conditions and with regard to all types of pulps and sometimes require the use of a
20 cationic promoter.

Surface sizing agents are known to a person skilled in the art and exist in the form of anionic dispersions. They are copiously described in the literature. They are synthesized by emulsion
25 polymerization using an anionic copolymer of low molecular mass as emulsifier. It is known to a person skilled in the art that the absence of surfactant

On the other hand, these anionic emulsions have certain disadvantages. In particular, they show little attachment to cellulose fibres which are slightly anionic, which causes recycling problems in closed circuits. A high dosage is necessary in order to obtain good sizing properties, because a portion of the dispersion does not remain at the surface and spreads throughout the thickness of the paper sheet. Furthermore, such anionic emulsions are not compatible with some starches, such as, for example, cationic starches.

Cationic dispersions have therefore been envisaged as sizing agents. Several methods of synthesis are possible. That which proves to be the most relevant and which the present invention relates to is emulsion polymerization using a cationic copolymer of low mass. Patent DE 2,454,397 claims the

during the synthesis and a very fine particle size are preferable in obtaining satisfactory effectiveness during the surface treatment. Patent US 08,434,600 discloses, for example, the emulsion synthesis from
5 styrene-acrylic acid copolymers used without cosurfactant to give emulsions with a particle size of 65 nm, while Patent FR 9606737 claims the use of dispersions with a size of approximately 55 nm synthesized using styrene-maleic anhydride (SMA)
10 copolymers.

On the other hand, these anionic emulsions have certain disadvantages. In particular, they show little attachment to cellulose fibres which are slightly anionic, which causes recycling problems in
15 closed circuits. A high dosage is necessary in order to obtain good sizing properties, because a portion of the dispersion does not remain at the surface and spreads throughout the thickness of the paper sheet. Furthermore, such anionic emulsions are not compatible
20 with some starches, such as, for example, cationic starches.

Cationic dispersions have therefore been envisaged as sizing agents. Several methods of synthesis are possible. That which proves to be the
25 most relevant and which the present invention relates to is emulsion polymerization using a cationic copolymer of low mass. Patent DE 2,454,397 claims the

use of oligomers based mainly on styrene and on dimethylaminoethyl acrylate which are synthesized in an organic solvent. Patent DE 3,401,573 claims the use of styrene, acrylonitrile and dimethylaminoethyl acrylate or methacrylate terpolymers. These two processes have the disadvantage of using an organic solvent which has to be removed before or after the emulsion polymerization. They are therefore neither economical nor ecological. Furthermore, there may be problems of stability of the emulsion at high temperatures typical of sizing baths or at a high shear gradient. Another patent, DE 4,200,715, claims the use of a hydrophobic modified cationic polyamidoamine. This process results in emulsions with a very low solids content and with particle sizes of about 160 nm. These emulsions are therefore neither economical nor effective in the present application.

According to the prior art, it therefore proves to be impossible to use, as sizing agent, cationic emulsions which have a high solids content, which have a fine particle size and which are synthesized without organic solvent or surfactant.

United States Patent US 3,444,151 discloses, however, the synthesis of imide derivatives (II) of copolymers based on maleic anhydride (I) and claims their use in emulsion polymerization for the purpose of latex synthesis. However, this patent claims the use of

compound (II) in a proportion of 2 to 20% by weight with respect to the monomers, which is in fact insufficient for the purpose of obtaining correctly stabilized latices in the absence of conventional
5 surfactant (the examples taken up in the patent are, moreover, all based on the joint use of conventional surfactant).

The present invention provides a simple process for the synthesis of cationic emulsions and for
10 the application of these emulsions to paper, which give much better results than the equivalent anionic emulsions.

The present invention is distinguished from the prior art in that it uses cationic emulsions of a
15 novel type which are intended to be used as sizing agent, which emulsions are obtained in the presence of imide derivatives (II) of copolymers based on maleic anhydride which are used in sufficient proportions to avoid recourse to conventional surfactants. The
20 emulsions thus synthesized have high hydrophobicity, a fine particle size, a high solids content, weak foaming and good mechanical stability, good stability towards freezing/thawing and good stability at high temperatures. They can be used equally well as surface
25 sizing agent and as internal sizing agent. In the surface application, they are compatible with a large number of starches. In the internal application, they

make possible immediate sizing without the use of a retention agent.

The invention therefore relates to the application, as sizing agents for papers, of cationic
 5 dispersions resulting from the emulsion polymerization of a mixture of mainly hydrophobic monomers in the presence of an aqueous solution of imide derivatives of copolymers based on maleic anhydride of low molecular mass and in the absence of conventional surfactant.
 10 Emulsion synthesis using these copolymers results in strongly hydrophobic cationic dispersions, with a high solids content and with a low particle size, which confer both very good hydrophobicity on the papers treated and good ink-jet printability.

15 One of the subject-matters of the invention is the aqueous dispersion of hydrophobic polymers which can be used alone or in combination with other agents as sizing agent for paper. It can be obtained according to the process described hereinbelow, which itself
 20 constitutes another subject-matter of the invention.

The process for producing the aqueous dispersion used as sizing agent for papers is carried out by emulsion polymerization starting from an imide derivative (II) of a copolymer based on maleic
 25 anhydride. The synthesis of these derivatives, based on the reaction of a diamine and of a polymer (I) based on maleic anhydride, is disclosed in Patent US 3,444,151.

make possible immediate sizing without the use of a retention agent.

The invention therefore relates to the application, as sizing agents for papers, of cationic
5 dispersions resulting from the emulsion polymerization of a mixture of mainly hydrophobic monomers in the presence of an aqueous solution of imide derivatives of copolymers based on maleic anhydride of low molecular mass and in the absence of conventional surfactant.
10 Emulsion synthesis using these copolymers results in strongly hydrophobic cationic dispersions, with a high solids content and with a low particle size, which confer both very good hydrophobicity on the papers treated and good ink-jet printability.

15 One of the subject-matters of the invention is the aqueous dispersion of hydrophobic polymers which can be used alone or in combination with other agents as sizing agent for paper. It can be obtained according to the process described hereinbelow, which itself
20 constitutes another subject-matter of the invention.

The process for producing the aqueous dispersion used as sizing agent for papers is carried out by emulsion polymerization starting from an imide derivative (II) of a copolymer based on maleic
25 anhydride. The synthesis of these derivatives, based on the reaction of a diamine and of a polymer (I) based on maleic anhydride, is disclosed in Patent US 3,444,151.

Briefly, these imide derivatives are obtained by reaction between a polymer (I) and a primary tertiary diamine, for example dimethylpropylenediamine (DMAPA), preferably by a bulk process. The primary amine
5 functional group will react with the anhydride functional group to form an amic acid and then this ring will reclose to form an imide derivative (II) of the polymer (I). The amine derivatives used in this invention are preferably those of the type I disclosed
10 in Patent US 3,444,151, that is to say those where a diamine reacts completely with the anhydride functional group with a molar ratio of 1 to 1. The use of copolymers exhibiting residual anhydride or acid functional groups, resulting from a reaction with a
15 deficiency of amine, is also possible.

The polymer (I) can be a copolymer or a terpolymer composed of maleic anhydride and of hydrophobic monomers chosen from α -olefins, unsaturated ethylenic aromatics, vinyl ethers or allyl ethers. The
20 preferred copolymer of the invention is a copolymer of styrene and of maleic anhydride (SMA) with a styrene to maleic anhydride ratio of 1/1 to 6/1, preferably of 2/1 to 4/1. The number-average molecular mass of the emulsifying copolymer is between 500 and 20,000,
25 preferably between 2000 and 5000. The percentage by mass of this oligomer in the final dry matter is between 10% and 40%, preferably between 20% and 30%.

The polymer (I) will preferably be chosen from copolymers of styrene and of maleic anhydride having acid numbers ranging from 500 to 200 mg KOH/g and sold by the company Elf Atochem under the names of
5 SMA® 1000, SMA® 2000, SMA® 3000, SMA® EF30, and SMA® EF40 and SMA® EF60.

After imidization, the copolymer is subsequently dissolved in aqueous solution and neutralized with an acid to give a cationic emulsifying
10 oligomer. The acid used will preferably be a volatile weak acid, such as ethanoic or methanoic acid.

The cationic emulsion is then synthesized, using conventional techniques for emulsion polymerization, in an aqueous solution comprising an
15 appropriate amount, preferably 30 to 50% with respect to the monomers, of the cationic emulsifier (II) described above and without addition of conventional macromolecular surfactant, in the presence of a conventional radical initiating system and of a mixture
20 of ethylenically unsaturated monomers, for example composed of styrene and of (meth)acrylic esters.

The radical initiator can be a water-soluble initiator, such as ammonium, potassium or sodium persulphates, optionally used in combination with a
25 reducing agent of sodium metabisulphite type, or alternatively hydrogen peroxide or a hydroperoxide, such as tert-butyl hydroperoxide, in combination with a

reducing agent, such as ascorbic acid or sodium formaldehydesulphoxylate. This initiator can also be soluble in organic media, such as azo derivatives, for example azobisisobutyronitrile, or organic peroxides.

5 The polymerization temperature is between 30°C and 100°C, preferably between 60°C and 90°C, and will be adjusted to the initiating system used.

 The monomers are chosen in particular so as to obtain the desired glass transition temperature (T_g)
10 but also the desired polarity, the desired functionality or the desired degree of cross-linking. This T_g can be between -70°C and 100°C, preferably between 0°C and 50°C.

 By way of example, the monomers will be
15 chosen from methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate and more generally alkyl (meth)acrylates of formula:

$$\text{CH}_2=\text{C}(\text{R}_1)\text{COOR}_2$$
, with $\text{R}_1=\text{H}$ or CH_3 and R_2 a group comprising 1 to 22 C,

20 perfluoroalkyl (meth)acrylates of formula:

$$\text{CH}_2=\text{C}(\text{R}_1)\text{COO}-(\text{CH}_2)_n-\text{C}_{n'}\text{F}_{2n'+1}$$
, with $\text{R}_1=\text{H}$ or CH_3 ,
 $n=1-4$ and $n'=1-14$,

 vinyl acetate, styrene, versatic esters, acrylic acid, methacrylic acid, acrylamide, ethylene
25 glycol dimethacrylate, and the like.

 The cationic dispersions of the invention have a solids content of between 20% and 50%,

preferably between 40% and 50%, and a particle size of between 50 nm and 300 nm with a mean particle size preferably of less than 100 nm. They have very good compatibility with the starches liable to be used in the size press, even at high temperature, whether these are native starches, weakly anionic starches or cationic starches. They have a low viscosity, preferably of less than 100 mPa·s for a solids content of 41%. They have very good stability over time, very good mechanical stability and very good resistance to the freezing/thawing cycle. They confer very good hydrophobicity on the papers treated, at treatment levels far below those of an equivalent anionic emulsion. In particular, they make possible the surface treatment of papers of test liner type intended for board packing, where the papers are required to have very good hydrophobicity. They also make it possible to use, inter alia, a starch and pigments which are cationic during the surface treatment of the paper and to obtain very good ink-jet printability. This is because the particles present in the printing inks are generally anionic and will attach more easily to the surface of the paper if cationic components are present.

Processes for the treatment of paper by external or internal sizing are described in the applicational examples.

Examples

The following examples illustrate the invention without limiting the scope thereof.

5 **Synthesis examples**

Example 1:

Synthesis of the cationic surface-active agent

10 This example describes the process for the synthesis of an imide derivative of a styrene-maleic anhydride copolymer denoted by SMA.

 Dimethylpropylenediamine (DMPA) and then SMA are first of all introduced, at ambient temperature, into an electrically heated two-litre reactor equipped
15 with a stirring device suitable for viscous media. The reaction mixture is then heated to 150°C before starting the stirring and is then brought to 200°C. From this moment on, stationary conditions are maintained for 75 minutes before the imidized SMA is
20 extruded via the bottom valve of the reactor into a liquid nitrogen bath. The imidized SMA obtained is subsequently milled.

 For Example S1-1, the reaction mixture comprises 170 g of DMPA and 830 g of an SMA copolymer
25 composed of 79.8% by mass of styrene and 20.2% by mass of maleic anhydride with a number-average molecular

mass of 3000 (commercially available under the name of SMA® EF40 from Elf Atochem S.A.).

A powdered copolymer S1-1 is obtained, the characteristics of which are as follows:

- 5 Residual DMAPA = 600 ppm
 Tg = 112°C
 Acid number = 7.5 mg KOH/g.
 Examples S1-2, S1-3 and S1-4

10 The same type of test can be carried out with other copolymers of styrene and of maleic anhydride exhibiting other styrene/maleic anhydride ratios, the nature of the products employed, the amounts used and the final characteristics of the products obtained being summarized in the following table:

15

| Reference | S1-2 | S1-3 | S1-4 |
|-------------------------------|-----------|-----------|-----------|
| SMA nature | SMA® 1000 | SMA® 2000 | SMA® 3000 |
| Amount of SMA (g) | 690 | 760 | 800 |
| Amount of DMAPA (g) | 310 | 240 | 200 |
| Acid number (mg KOH/g) | 7 | 2.6 | 10.6 |
| Level of residual DMAPA (ppm) | 600 | 600 | 600 |
| Tg (°C) | 82 | 80 | 91 |

Example 2:

Dissolution of the cationic surfactant (SUR)

171 g of the SUR S1-1, 644 g of water and 39 g of glacial acetic acid are introduced into a three-necked glass reactor with a capacity of 1 litre equipped with a central stirrer, a condenser, a temperature probe and a device for introducing acetic acid. The combined reactants are heated to 60°C and kept stirring until the oligomer has completely dissolved.

The aqueous solution S2-1 obtained has an S1-1 concentration of approximately 20%. The dissolution of the SUR can optionally be carried out directly in the polymerization reactor as a preliminary stage of Example S3-1.

Example 3:Synthesis of the cationic dispersion

This example describes the synthesis of a cationic dispersion according to the invention.

642 g of aqueous solution S2-1 comprising 20% of oligomer S1-1 are introduced into a jacketed glass reactor with a capacity of 1 litre equipped with a central stirrer, a condenser, a temperature probe and a device for continuously introducing an initiator solution and a mixture or pre-emulsion of monomers, and the reaction mixture is brought to 85°C.

Furthermore, an initiator solution is prepared by dissolving 3 g of ammonium persulphate in

60 g of demineralized water, and a mixture of monomers is prepared composed of 138 g of styrene and 162 g of butyl acrylate.

When the reaction mixture is at 85°C, the
5 initiator solution and the mixture of monomers are fed in over a period of 2 hours, with stirring and while maintaining the temperature at 85°C.

The reaction mixture is then kept stirring for an additional two hours at 85°C, then cooled to
10 ambient temperature, filtered through a 100 µm cloth and drained to result in the S3-1 dispersion, which exhibits the following characteristics.

Solids content = 41%

Viscosity is 35 mPa·s, measured using a
15 Brookfield device at 25°C according to the Standard

pH = 4

Mean diameter of the particles = 95 nm

Tg = 25°C

Comparative Example 1

20 A sizing agent is synthesized in the same way as that disclosed in Example 1 of Patent FR 9606737, to give an anionic emulsion S4 stabilized by a styrene-maleic anhydride copolymer neutralized with ammonia, composed of 74.3% by mass of styrene and 25.7% by mass
25 of maleic anhydride. This emulsion is therefore the anionic equivalent of the emulsion S3-1.

This emulsion S4 exhibits the following characteristics:

Solids content = 23.5%

Brookfield viscosity at 25°C = 20 mPa·s

5 pH = 8.85

Mean diameter of the particles = 55 nm

Tg = 25°C

Applicational examples

Three papers are surface treated using a
10 laboratory-scale size press.

The first two, of printing and writing type, have a grammage of 80 g/m² and are sized with alkyl ketene dimer (Aquapel® 315 from Hercules, hereinafter AKD) at a level of 0.2% or 0.6% with respect to the
15 weight of the paper.

Another paper of the test liner type intended to be used for the packing board application has a grammage of 130 g/m² and was not subjected to any internal sizing.

20 The following two tests were carried out in order to measure the hydrophobicity and the resistance to penetration by aqueous solutions of the papers treated:

Cobb test: this test is well known to a
25 person skilled in the art and is described in NF Standard EN 20535-ISO 535. The amount of water absorbed after a given time is given in g/m². In this

instance, the Cobb test is carried out with a contact time of 60 seconds (Cobb₆₀) or of 30 minutes (Cobb₁₈₀₀).

HST test: this test is carried out according to Tappi Test Methods T Standard 530 OM-96. The papers to be tested have a size of 6 × 6 cm and are subjected, on one face, to a green ink (prepared with 1.25% of Naphthol Green B dye, 1% of formic acid and the remaining percentage of demineralized water). The penetration time of the aqueous ink is determined by reflection of a light source on the opposite face when the percentage of reflection reaches 80%.

Example A1

This example shows the advantage of the sizing agents according to the invention in the surface treatment of printing and writing papers with regard to their resistance to water and to penetration of the ink. An acceptable printing and writing paper must have a Cobb₆₀ of less than 30 and an HST of greater than 100.

The paper treated with 0.2% of AKD is surface sized with an aqueous solution comprising:

3% by weight of weakly anionic starch Amylis®
100 P (Roquette)

0.25% and 0.5% by weight of active material
of the emulsions S3-1 and S4

The solution being brought to 100% by addition of the necessary complementary demineralized water.

5

Example A2

15 3% by weight of cationic starch Catosize® 240
(National Starch)

The solution being brought to 100% by
20 addition of the necessary complementary demineralized
water.

The following results, in comparison with those of Example A1, clearly show the compatibility of the dispersion according to the invention with any type of starch. Whereas the properties of the emulsion S3-1 are reinforced in the presence of a cationic starch, those of the emulsion S4 decline and are even inferior to those of the starch alone for the paper with 0.6% of AKD, due to an incompatibility in the sizing slip.

10 Paper with 0.2% of AKD

| Products | Starch alone | S3-1 | S4 |
|--|--------------|------|----|
| Cobb ₆₀ (g/m ²) | 100 | 20.7 | 65 |
| HST (s) | 0 | 300 | 8 |

Paper with 0.6% of AKD

| Products | Starch alone | S3-1 | S4 |
|--|--------------|------|------|
| Cobb ₆₀ (g/m ²) | 52.5 | 19.5 | 59.5 |
| HST (s) | 9 | 120 | 7 |

15

Example A3

This example shows the advantage of the sizing agents according to the invention in the surface treatment of packing board papers, with regard to their resistance to water. For these papers, very good

20

resistance to water is required over long periods of time. An acceptable paper of test liner type intended for packing board must have a Cobb₁₈₀₀ equal to or less than 120.

5 The paper of test liner type described above is surface sized with a solution comprising:
 8% by weight of weakly anionic starch Amylis®
 100 P (Roquette)

 0.7% and 1.2% by weight of active material of
 10 the emulsions S3-1 and S4

 The solution being brought to 100% by addition of the necessary complementary demineralized water.

 The following results demonstrate the
 15 possibility of treating, with reasonable amounts of sizing agent according to the invention, papers of test liner type which have not been subjected to any internal sizing.

| Products | Starch alone | S3-1 0.7% | S3-1 1.2% | S4 0.7% | S4 1.2% |
|---|-----------------|-----------|-----------|---------|---------|
| Cobb ₆₀ (g/m ²) | 200 | 30 | 20 | 61 | 28 |
| Cobb ₁₈₀₀ (g/m ²) | 250 | 150 | 105 | 165 | 150 |

Example A4

This example describes the use of the cationic dispersion of the invention as internal sizing agent.

5 The paper is obtained according to the process which consists in preparing handsheets on a Franck device starting from a pulp beaten to a certain Schopper-Riegler degree of drainability (see NF Standard Q 50003). The sizing agent is added to the
10 fibrous suspension composed of 5 g/l of fibres in water. Stirring is continued for 3 minutes. The handsheet is prepared at a mean grammage of 65 g/m², after draining, dewatering and drying for 5 minutes at 95°C. The pulp used in this instance is composed of 50%
15 short fibres and 50% long fibres and has a Schopper-Riegler degree of 25.

1% of sizing agent with respect to the dry fibrous matter is added. The sizing agents used are emulsions S3-1 and S4, as well as AKD (Aquapel® 315
20 from Hercules). The handsheets treated with AKD are subjected to accelerated maturing in an oven for 10 minutes at 110°C.

| Sizing agent | None | AKD | S3-1 | S4 |
|--------------------|-------|-----|------|-------|
| Cobb ₆₀ | > 100 | 42 | 24 | > 100 |

As is seen in the light of these results, the emulsion S3-1 gives entirely satisfactory sizing results without a retention agent, whereas the performance is mediocre with AKD used alone.

- 5 Furthermore, no maturing stage is necessary. The anionic emulsion does not give any result because it is not attached to the fibres.

CLAIMS

1. Process for producing an aqueous cationic dispersion of polymers with a hydrophobic nature based on the emulsion polymerization at a temperature ranging from 30 to 100°C of at least one emulsion-polymerizable monomer in the presence of 20 to 60% by weight, with respect to the monomer(s), of an imidized styrene/maleic anhydride copolymer acting as sole surfactant, the solids content of the dispersion being from 20 to 50%.

2. Process according to Claim 1, characterized in that the styrene and the maleic anhydride are taken in a ratio of 1/1 to 6/1 and preferably of 2/1 to 4/1.

3. Process according to Claim 1 or 2, characterized in that the said copolymer has a number-average molecular mass of between 500 and 20,000 and preferably between 2000 and 5000.

4. Process according to one of the preceding claims, characterized in that the degree of imidization of the said copolymer is between 50 and 100%.

5. Process according to one of the preceding claims, characterized in that the said copolymer is imidized by dimethylpropylenediamine.

6. Process according to any one of the preceding claims, characterized in that the monomer is chosen from the groups comprising:

- hydrophobic monomers, such as methyl
5 acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate and more generally alkyl (meth)acrylates of formula:

$\text{CH}_2=\text{C}(\text{R}_1)\text{COOR}_2$, with $\text{R}_1=\text{H}$ or CH_3 and R_2 a group comprising 1 to 22 C,

10 perfluoroalkyl (meth)acrylates of formula:

$\text{CH}_2=\text{C}(\text{R}_1)\text{COO}-(\text{CH}_2)_n-\text{C}_{n'}\text{F}_{2n'+1}$, with $\text{R}_1=\text{H}$ or CH_3 ,
 $n=1-4$ and $n'=1-14$,

vinyl acetate, styrene or versatic esters,

- relatively hydrophilic monomers, such as
15 acrylic acid, methacrylic acid, acrylamide or ethylene glycol (meth)acrylate.

7. Cationic dispersion of polymers with a hydrophobic nature as can be had by the process of Claims 1 to 6, characterized in that the polymer
20 particles have a size of between 50 and 500 nm and preferably of less than 300 nm.

8. Dispersion according to Claim 7, characterized in that the polymer with a hydrophobic nature has a glass transition temperature of between
25 -70°C and 100°C and preferably between 0 and 50°C .

9. Use of the dispersion according to Claim 7 or 8 as internal sizing agent in the treatment of papers and boards.

10. Use of the dispersion according to Claim 7 or 8 in combination with other sizing agents, such as starch, in the surface sizing of papers and boards.

11. Composition for the external sizing of papers and boards comprising the dispersion according to either of Claims 7 and 8 and starch taken in a ratio by mass ranging from 5 to 50%.

(12) DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DU TRAITÉ DE COOPÉRATION
EN MATIÈRE DE BREVETS (PCT)(19) Organisation Mondiale de la Propriété
Intellectuelle
Bureau international(43) Date de la publication internationale
28 décembre 2000 (28.12.2000)

PCT

(10) Numéro de publication internationale
WO 00/78818 A1(51) Classification internationale des brevets⁷: C08F 2/28(74) Mandataire: SARRAF, Tarek; ATOFINA, Cours
Michelet - La Défense 10, F-92091 Paris La Défense
Cedex (FR).

(21) Numéro de la demande internationale:

PCT/FR00/01692

(22) Date de dépôt international: 20 juin 2000 (20.06.2000)

(25) Langue de dépôt: français

(26) Langue de publication: français

(30) Données relatives à la priorité:

99/07910

21 juin 1999 (21.06.1999) FR

(71) Déposant (pour tous les États désignés sauf US): ATO-
FINA [FR/FR]; 4/8, cours Michelet, F-92800 Puteaux
(FR).(81) États désignés (national): AE, AG, AL, AM, AT, AU, AZ,
BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK,
DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID,
IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT,
LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ,
PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT,
TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.(84) États désignés (régional): brevet ARIPO (GH, GM, KE,
LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), brevet eurasien
(AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), brevet européen
(AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU,
MC, NL, PT, SE), brevet OAPI (BF, BJ, CF, CG, CI, CM,
GA, GN, GW, ML, MR, NE, SN, TD, TG).

(72) Inventeurs; et

(75) Inventeurs/Déposants (pour US seulement): BETREM-
IEUX, Isabelle [FR/FR]; 14, Côte d'Harcourt, F-27170
Beaumontel (FR). DUMOUSSEAUX, Christophe
[FR/FR]; 6, avenue des Chardons, F-94800 Villejuif (FR).
VERGE, Christophe [FR/FR]; 14, Côte d'Harcourt,
F-27170 Beaumontel (FR). FERET, Bruno [FR/FR];
8, rue Legendre, F-95210 Saint-Gratien (FR). FLAT,
Jean-Jacques [FR/FR]; 5, parc Maubuisson, F-27470
Serquigny (FR).

Publiée:

- Avec rapport de recherche internationale.
- Avant l'expiration du délai prévu pour la modification des revendications, sera republiée si des modifications sont reçues.

En ce qui concerne les codes à deux lettres et autres abréviations, se référer aux "Notes explicatives relatives aux codes et abréviations" figurant au début de chaque numéro ordinaire de la Gazette du PCT.

(54) Title: HYDROPHOBIC CATIONIC DISPERSIONS STABILISED BY LOW MOLECULAR WEIGHT MALEIMIDE COPOLYMERS, FOR PAPER SIZING

(54) Titre: DISPERSIONS CATIONIQUES HYDROPHOBES STABILISEES PAR DES COPOLYMERES MALEIMIDES DE FAIBLE MASSE MOLECULAIRE, POUR LE COLLAGE DU PAPIER

(57) Abstract: The invention concerns a method for obtaining an aqueous dispersion of hydrophobic polymers dispersed in the form of particles with mean diameter less than 100 nm stabilised solely with a macromolecular surfactant based on low molecular weight styrene/maleic anhydride imide copolymer. The invention also concerns the use of said dispersion for treating and sizing paper.

(57) Abrégé: L'invention décrit un procédé nouveau pour l'obtention d'une dispersion aqueuse de polymères hydrophobes dispersés sous la forme de particules de diamètre moyen inférieur à 100 nm stabilisées uniquement par un tensio-actif macromoléculaire à base de copolymère styrène / anhydride maléique imidisé de faible masse. L'invention décrit aussi l'utilisation d'une telle dispersion dans le traitement et le collage du papier.

WO 00/78818 A1



10/019161

01 MAR 2002

PTO/SB/01 (10-01)

Approved for use through 10/31/2002. OMB 0651-0032

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

**DECLARATION FOR UTILITY OR
DESIGN
PATENT APPLICATION
(37 CFR 1.63)**Declaration
Submitted
with Initial
Filing

OR

Declaration
Submitted after Initial
Filing (surcharge
(37 CFR 1.16 (e))
required)**Attorney Docket Number**

119464

First Named Inventor

Betremieux

COMPLETE IF KNOWN**Application Number**

10 / 019161

Filing Date

12/19/01

Art Unit**Examiner Name****As the below named inventor, I hereby declare that:**

My residence, mailing address, and citizenship are as stated below next to my name.

I believe I am the original and first inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**HYDROPHOBIC CATIONIC DISPERSION STABILIZED BY MALEIMIDE COPOLYMERS
OF LOW MOLECULAR MASS, FOR THE SIZING OF PAPER**

(Title of the Invention)

the specification of which



is attached hereto

OR



was filed on (MM/DD/YYYY)

06/20/2000

as United States Application Number or PCT International

Application Number

PCT/FR00/01692

and was amended on (MM/DD/YYYY)

(if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or (f), or 365(b) of any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent, inventor's or plant breeder's rights certificate(s), or any PCT international application having a filing date before that of the application on which priority is claimed.

| Prior Foreign Application Number(s) | Country | Foreign Filing Date (MM/DD/YYYY) | Priority Not Claimed | Certified Copy Attached? | |
|--|---------|-------------------------------------|--------------------------|--------------------------|-------------------------------------|
| | | | | YES | NO |
| PCT/FR00/01692 9907910 | FRANCE | 06/20/2000 06/21/1999 | <input type="checkbox"/> | <input type="checkbox"/> | <input checked="" type="checkbox"/> |
| | | | <input type="checkbox"/> | <input type="checkbox"/> | <input checked="" type="checkbox"/> |
| | | | <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |
| | | | <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |

☐ Additional foreign application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto:

(Page 1 of 3)

Burden Hour Statement. This form is estimated to take 21 minutes to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington, DC 20231.



10015161 030102

PTO/SB/01 (10-01)

Approved for use through 10/31/2002. OMB 0651-0032

U.S. Patent and Trademark Office, U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

DECLARATION — Utility or Design Patent ApplicationDirect all correspondence to: ☒Customer Number
or Bar Code LabelOR ☐

Correspondence address below

26316

PATENT TRADEMARK OFFICE

Name

Address

City

State

ZIP

Country

Telephone

Fax

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

NAME OF SOLE OR FIRST INVENTOR :



A petition has been filed for this unsigned inventor

Given Name
(first and middle [if any]) IsabelleFamily Name
or Surname BETREMIEUXInventor's
Signature

FRX

Date 4/01/2002

Residence: City Cote la Foret

State

Country FRANCE

Citizenship French

Mailing Address 36 Avenue de la gare

City Cote la Foret

State

ZIP 60580

Country France

NAME OF SECOND INVENTOR :



A petition has been filed for this unsigned inventor

Given Name
(first and middle [if any]) ChristopheFamily Name
or Surname DUMOUSSEAUInventor's
Signature

Date 2002

Residence: City Villejuif

State

Country France

Citizenship French

Mailing Address 6, Avenue des Chardons

City Villejuif

State

ZIP 94800

Country France



Additional inventors are being named on the 1 supplemental Additional Inventor(s) sheet(s) PTO/SB/02A attached hereto

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

DECLARATION — Utility or Design Patent ApplicationDirect all correspondence to: ☒Customer Number
or Bar Code LabelOR ☐

Correspondence address below

26316

PATENT/TRADEMARK OFFICE

Name

Address

City

State

ZIP

Country

Telephone

Fax

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

NAME OF SOLE OR FIRST INVENTOR :

☐ A petition has been filed for this unsigned inventor

Given Name

(first and middle [if any]) Isabelle

Family Name
or Surname

BETREMIEUX

Inventor's
Signature

Date /01/2002

Residence: City

Coye la Foret

State

Country FRANCE

Citizenship French

Mailing Address 36 Avenue de la gare

City Coye la Foret

State

ZIP 60580

Country France

NAME OF SECOND INVENTOR:

☐ A petition has been filed for this unsigned inventor

Given Name

(first and middle [if any]) Christophe

Family Name
or Surname

DUMOUSSEAUX

Inventor's
Signature

FRX

Date 1/18/2002

Residence: City

Villejuif

State

Country France

Citizenship French

Mailing Address 6, Avenue des Chardons

City Villejuif

State

ZIP 94800

Country France



Additional inventors are being named on the 1 supplemental Additional Inventor(s) sheet(s) PTO/SB/02A attached hereto



1003151 030107

Please type a plus sign (+) inside this box → ☐PTO/SB/02A (3-97)
Approved for use through 9/30/98 OMB 0651-0032
Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

DECLARATION

ADDITIONAL INVENTOR(S)
Supplemental Sheet
Page 1 of 3

| | | | |
|---|-----------------------|---|--------------------------|
| Name of Additional Joint Inventor, if any: | | <input type="checkbox"/> A petition has been filed for this unsigned inventor | |
| Given Name (first and middle [if any]) | | Family Name or Surname | |
| Christophe | | VERGE | |
| Inventor's Signature | | | Date 14/01/2002 |
| Residence: City | Coye la Foret | State | Country France |
| Post Office Address | 36 Avenue de la gare | | |
| Post Office Address | | | |
| City | Coye la Foret | State | ZIP 60580 Country France |
| Name of Additional Joint Inventor, if any: | | <input type="checkbox"/> A petition has been filed for this unsigned inventor | |
| Given Name (first and middle [if any]) | | Family Name or Surname | |
| Bruno | | FERET | |
| Inventor's Signature | | | Date /01/2002 |
| Residence: City | Saint Gratien | State | Country France |
| Post Office Address | 8, rue Legendre | | |
| Post Office Address | | | |
| City | Saint Gratien | State | ZIP 95210 Country France |
| Name of Additional Joint Inventor, if any: | | <input type="checkbox"/> A petition has been filed for this unsigned inventor | |
| Given Name (first and middle [if any]) | | Family Name or Surname | |
| Jean-Jacques | | FLAT | |
| Inventor's Signature | | | Date /01/2002 |
| Residence: City | Serquigny | State | Country France |
| Post Office Address | 5, parc de Maubuisson | | |
| Post Office Address | | | |
| City | Serquigny | State | ZIP 27470 Country France |

Burden Hour Statement: This form is estimated to take 0.4 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington, DC 20231.



10019161 030102

Please type a plus sign (+) inside this box → ☐

PTO/SB/02A (3-97)

Approved for use through 9/30/98. OMB 0651-0032

Patent and Trademark Office; U S DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number

**DECLARATION****ADDITIONAL INVENTOR(S)**
Supplemental Sheet
Page 32 of 3**Name of Additional Joint Inventor, if any:**☐ A petition has been filed for this unsigned inventor

Given Name (first and middle [if any])

Family Name or Surname

Christophe

VERGE

Inventor's
Signature

Date

/01/2002

Residence: City

Coye la Foret

State

Country

France

Citizenship

French

Post Office Address

36 Avenue de la gare

Post Office Address

City

Coye la Foret

State

ZIP

60580

Country

France

Name of Additional Joint Inventor, if any:☐ A petition has been filed for this unsigned inventor

Given Name (first and middle [if any])

Family Name or Surname

Bruno

FERET

Inventor's
Signature

Date

10/01/2002

Residence: City

Saint Gratien

State

Country

France

Citizenship

French

Post Office Address

8, rue Legendre

Post Office Address

City

Saint Gratien

State

ZIP

95210

Country

France

Name of Additional Joint Inventor, if any:☐ A petition has been filed for this unsigned inventor

Given Name (first and middle [if any])

Family Name or Surname

Jean-Jacques

FLAT

Inventor's
Signature

Date

/01/2002

Residence: City

Serquigny

State

Country

France

Citizenship

French

Post Office Address

5, parc de Maubuisson

Post Office Address

City

Serquigny

State

ZIP

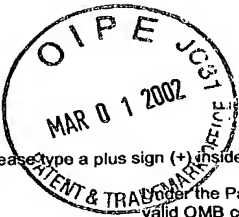
27470

Country

France

Burden Hour Statement This form is estimated to take 0.4 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington, DC 20231.





Please type a plus sign (+) inside this box → ☐

PTO/SB/02A (3-97)
Approved for use through 9/30/98 OMB 0651-0032
Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

+

| | |
|--------------------|---|
| DECLARATION | ADDITIONAL INVENTOR(S) Supplemental Sheet Page <u>3</u> of <u>3</u> |
|--------------------|---|

| | | | | | | | |
|---|-----------------------|-------|--|---|--------|-------------|------------|
| Name of Additional Joint Inventor, if any: | | | | <input type="checkbox"/> A petition has been filed for this unsigned inventor | | | |
| Given Name (first and middle [if any]) | | | | Family Name or Surname | | | |
| Christophe | | | | VERGE | | | |
| Inventor's Signature | | | | | | Date | /01/2002 |
| Residence: City | Coye la Foret | State | | Country | France | Citizenship | French |
| Post Office Address | 36 Avenue de la gare | | | | | | |
| Post Office Address | | | | | | | |
| City | Coye la Foret | State | | ZIP | 60580 | Country | France |
| Name of Additional Joint Inventor, if any: | | | | <input type="checkbox"/> A petition has been filed for this unsigned inventor | | | |
| Given Name (first and middle [if any]) | | | | Family Name or Surname | | | |
| Bruno | | | | FERET | | | |
| Inventor's Signature | | | | | | Date | /01/2002 |
| Residence: City | Saint Gratien | State | | Country | France | Citizenship | French |
| Post Office Address | 8, rue Legendre | | | | | | |
| Post Office Address | | | | | | | |
| City | Saint Gratien | State | | ZIP | 95210 | Country | France |
| Name of Additional Joint Inventor, if any: | | | | <input type="checkbox"/> A petition has been filed for this unsigned inventor | | | |
| Given Name (first and middle [if any]) | | | | Family Name or Surname | | | |
| Jean-Jacques | | | | FLAT | | | |
| Inventor's Signature | | | | | | Date | 11/01/2002 |
| Residence: City | Serquigny | State | | Country | France | Citizenship | French |
| Post Office Address | 5, parc de Maubuisson | | | | | | |
| Post Office Address | | | | | | | |
| City | Serquigny | State | | ZIP | 27470 | Country | France |

Burden Hour Statement. This form is estimated to take 0.4 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington, DC 20231

+